Fundamental Properties of MxP (M = Ti, V, Fe; x = 2, 3) Binary and Ternary Compounds

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1. Introduction

The magnetic and structural properties of 3d transition metal phosphides are of considerable interest. For example, the crystal structure of Fe_3P belong to the Ni_3P-type which has the space group $I\bar{4}$, eight formula units in a tetragonal unit cell and three crystallographically different Fe atom sites (denoted as FeI, FeII, and FeIII) [1]. In addition, the magnetic ground state of Fe_3P compound is a ferromagnetic (FM) with a high Curie temperature of 692 K and saturation magnetic moment of 1.89 μB/Fe atom at 10 K [2]. From Mössbauer and neutron diffraction measurements, the magnetic moments of FeI, FeII, and FeIII have been estimated to be 2.12, 1.25, and 1.83 μB, respectively [3]. As a same space group with Fe_3P, Mn_3P compound is antiferromagnetic (AFM) with the Néel temperature about 115 K, and Ni_3P and Cr_3P compounds show the Pauli-type paramagnetism [4]. The Co_3P phase does not exist in the binary system [5]. On the other hand, the other 3d transition metal phosphides, namely Ti_3P and V_3P, known to be Ti_3P-type (space group $P4_2/n$) crystal structure [6]. Here, we investigated fundamental magnetic and structural properties of MxP (M = Ti, V, Fe; x = 2, 3) binary and ternary compounds using the highly precise all-electron full-potential linearized augmented plane wave (FLAPW) method [7] based on density functional theory.

2. Computational Method and Models

The Perdew-Burke-Ernzerhof form of the generalized gradient approximation (GGA) [8] for the exchange correlation potential was used. An energy cutoff of 5.0 ($2\pi/a$), where a is the lattice parameter, was employed for expanding the linearized augmented plane wave basis set. An 18 ($2\pi/a$) star function cutoff was used for depicting the charge density and potential in the interstitial regions. Lattice harmonics with $l \leq 12$ were employed to expand the charge density, potential, and wave functions inside each muffin-tin sphere, with radii of 2.2 ~ 2.3 a.u. and 1.9 a.u. for 3d transition metals and P atoms, respectively. Integrations inside the Brillouin zone (BZ) were performed using the improved tetrahedron method over a 5×5×9 mesh within the three-dimensional (3D) BZ.

3. Results and Discussions

From the total energy calculations, we determined the equilibrium lattice constants and volue of M_3P and M_2P as shown in Table I. One can see that the calculated volume of Ti phosphides is the largest in the considered systems since the ionic radius of Ti is larger than the other elements. We also confirm that the lattice constants of these compounds are well consistent with experimentally estimated values. From magnetic point of view, it

is interesting found out that only iron phosphides system have magnetism, which the ground magnetic state was investigated by calculating the total energy with the nonmagnetic (NM) and FM states. As a result, the FM state of Fe_3P compound is more stable than the NM one by energy difference of 809 meV/f.u. Furthermore, the calculated magnetic moments of Fe_3P compound were calculated to be 2.367, 1.665, and 2.104 μB for FeI, FeII, and FeIII atoms, respectively. Overall the magnitudes of magnetic moments are rather overestimated compared to the neutron diffraction measurement [3]. The magnetic moment of P atom is coupled negatively to Fe atoms, even though its magnitude is small.

Table I. The calculated equilibrium lattice constant a (in Å) and volume V0 (in Å3/f.u.) of M_3P and M_2P compounds.

	System	Space Group	Magnetic State	a	c/a	V0
M3P	Ti_3P	$P4_2/n$	NM	9.989	0.501	62.42
	V_3P	$P4_2/n$	NM	9.360	0.508	52.07
	Fe_3P	$I\bar{4}$	FM	9.039	0.486	44.86
M2P	Ti_2P	$P\bar{6}2m$	NM	6.555	0.528	44.93
	V_2P	$P\bar{6}2m$	NM	6.428	0.500	38.32
	Fe_2P	$P\bar{6}2m$	FM	5.821	0.591	33.68

4. Summary

In this study, the fundamental properties of M_xP (M = Ti, V, Fe; x = 2, 3) binary compounds were investigated in terms of the FLAPW method within GGA. The calculated lattice parameters are well consistent with experimental values. Among considered systems, only the FM state of Fe_xP compounds found to be more stable compared to the NM one. Discussion on the fundamental properties of M_xP ternary compounds also will be given.

5. References

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